CHROMIUM HEXAVALENT COMPOUNDS

First Listed in the *First Annual Report on Carcinogens*

CARCINOGENICITY

Chromium hexavalent compounds: calcium chromate (13765-19-0), chromium trioxide (1333-82-0), lead chromate (7758-97-6), strontium chromate (7789-06-2), and zinc chromate (13530-65-9) are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans (IARC S.7, 1987). An increased incidence of lung cancer has been observed among workers in both the bichromate-producing industry and chromate-pigment manufacturing. There is evidence of a similar risk among chromium platers and chromium-alloy workers. The incidences of cancers at other sites may also be increased in such populations. However, a clear distinction between the relative carcinogenicity of chromium compounds of different oxidation states or solubilities has been difficult to achieve. Recent studies of chromate-pigment makers and users, chrome platers, welders and chrome-alloy foundry workers have shed some light on this problem. For chromate-pigment makers and users, respiratory cancer excesses have usually been found. Chromium pigments are usually hexavalent and commonly include zinc, lead, or strontium chromate. Chrome platers have also been found to have excess lung cancer. Stainless steel welding involves the greatest exposure to hexavalent chromium, as well as to nickel, and one study of chromium-nickel alloy foundry workers showed a statistically significant excess of lung cancers. (For a discussion on the carcinogenicity of metals, see the Introduction, Inclusion of Substances).

An IARC Working Group reported that there is sufficient evidence of carcinogenicity of the following hexavalent chromium compounds: calcium chromate (13765-19-0), chromium trioxide (1333-82-0), lead chromate (7758-97-6), strontium chromate (7789-06-2), and zinc chromate (13530-65-9) in experimental animals (IARC V.2, 1973; IARC V.23, 1980; IARC S.4, 1982; IARC S.7, 1987). Calcium chromate produced bronchial carcinomas after implantation of an intrabronchial pellet in rats and injection-site sarcomas after intramuscular implantation in rats and mice and after intrapleural injection in rats. Bronchial carcinomas were produced in rats after intrabronchial implantation of strontium chromate and zinc chromate. Injection-site sarcomas were produced in rats and mice after intramuscular, intrapleural, and subcutaneous injections of chromite ore, strontium chromate, chromium trioxide, lead chromate, and zinc chromate, but few or no sarcomas were induced by barium chromate (10294-40-3), sodium chromate (7775-11-3), sodium dichromate (10588-01-9), or chromic acetate (1066-30-4).

PROPERTIES

Chromium is an odorless, steel-to-semi-gray, lustrous metal available as crystals or powder (99.97% purity). It is insoluble in hot and cold water, nitric acid, and aqua regia, but reacts with dilute sulfuric acid and hydrochloric acid. Calcium chromate occurs in the form of yellow monoclinic prisms. It is soluble in cold and hot water and reacts with acids and ethanol. Chromium trioxide is odorless, dark-purplish-to-red rhombic crystals that are deliquescent. It is soluble in alcohol, ethanol, sulfuric acid, and nitric acid. When heated to decomposition, chromium trioxide emits smoke and irritating fumes. Lead chromate occurs as yellow or orange monoclinic crystals that are insoluble in water, acetic acid, and ammonia but are soluble in acid and alkali. Lead chromate, when heated to decomposition, emits toxic fumes of lead. Basic lead chromate is a red amorphous or crystalline powder. It is insoluble in hot and cold water, reacts with most acid and alkali but not with acetic acid or ammonia, and emits very toxic fumes of lead when heated to decomposition. Strontium chromate occurs as monoclinic yellow crystals.

It is soluble in cold and hot water and reacts with hydrochloric acid, nitric acid, acetic acid, and ammonium salts. Zinc chromate occurs as lemon yellow prisms. It is insoluble in cold water and acetone, dissolves in hot water, and is soluble in acid and liquid ammonia.

USE

In 1987 and 1989, estimated consumption of chromium ferroalloys, metals, and other chromium-containing materials by end use was as follows: stainless and heat-resisting steel, 79%; full-alloy steel, 8%; superalloys, 3%; and other alloys, 10% (USDOI, 1988, 1990). The steel industry is the major consumer of chromium. Chromium is used as an alloying and plating element on metal and plastic substrates for corrosion resistance in chromium-containing and stainless steels and in protective coatings for automotive and equipment accessories. It is also used in nuclear and high-temperature research. Similarly, barium chromate and calcium chromate find use in high-temperature applications, e.g., barium chromate in safety matches and pyrotechnics and both are used in high-temperature batteries. In 1985, 39% of the chromium trioxide produced was used for metal plating and treatment, 44% was used in wood treatment and preservatives, and 11% was exported (Chem. Profile, 1985). Chromium trioxide is used in chromium plating and in the manufacture of chromated copper arsenate (NCI DCE, 1985c). Chromic acetate, sodium chromate, and potassium chromate are used in the textile industry. Basic trivalent chromic sulfate is used in the tanning industry (Leather Industries of America, Inc., personal communication). Chromium compounds also find applications as pigments for floor covering products, paper, cement, and asphalt roofing, and in coloring glass an emerald color (HSDB, 1997). Lead chromate is chrome yellow and a component of chrome orange and green; chromium trioxide is green cinnabar; and zinc chromate is zinc yellow (Kirk-Othmer V.6, 1979). Chromium phosphate, strontium chromate, calcium chromate, chromic acetate, and potassium chromate and dichromate are also used in pigments. Other uses for chromium and its compounds include organic chemical synthesis, photomechanical processing, and industrial water treatment. In medicine, chromium compounds are used in astringents and antiseptics (Sax, 1987).

PRODUCTION

Chromite has not been mined in the United States since 1961. Domestic deposits are small or of low grade. Chromite ore, however, is imported in large quantities averaging 164 million lb from 1992-1996 (Papp, 1996).

Chromium production and imports varied widely over a 15 year period from 1982-1996. Chromium production averaged 190 million lb for the time period 1982 through 1989 while imports averaged 711 million lb over the same time period. There was no US production from 1990 to 1996 while the average import for this period was 15 million lb. In 1996 US production and imports were 6.6 and 19.2 million lb respectively (Papp, 1996 and USDOI, 1985, 1987, 1988, and 1990).

The latest figures from the U.S. Geological Survey (Papp, 1996) show that about 2 million lb of zinc and lead chromate have been exported, mainly to Canada (96%). The total export volume for other chromates, dichromates, and peroxchromates as 903,895 lb in 1995 and 848,780 lb in 1996. The situation was practically reversed for imports. U.S. imports for consumption of lead and zinc chromates were 873,031 lb in 1995 and 251,327 lb in 1996, while imports of other chromates, dichromates, and peroxochromates were 2.0 and 1.3 million lb, respectively for each year.

EXPOSURE

The primary routes of potential human exposure to chromium and certain chromium compounds are inhalation, ingestion, and dermal contact. Chromium (in the form of unidentified chromium compounds) is widely distributed in air, water, soil, and food. In trace amounts, its trivalent form may be an essential ingredient in the diet. The entire population is possibly exposed to some of these compounds, but the levels of exposure vary. Hexavalent chromium [chromium(VI)] compounds are of greater health concern than trivalent chromium compounds [chromium(III)], but hexavalent compounds are readily reduced to trivalent forms in the presence of organic matter.

NIOSH has found that certain forms of chromium(VI) are noncarcinogenic; they are the monochromates and dichromates of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium(VI) oxide (chromic acid anhydride) (NIOSHb, 1979b). The National Occupational Hazard Survey, conducted by NIOSH from 1972 to 1974, estimated that 2.5 million workers were possibly exposed to chromium and its compounds in the workplace (NIOSH, 1976). NIOSH estimated that 175,000 workers were potentially exposed to chromium(VI), which is produced principally from chromite ore (NIOSHb, 1979b). The National Occupational Exposure Survey (NOES) (1981-1983) estimated that a total of 115,788 workers, including 3,101 women, were potentially exposed to chromium; 6,339 total workers were potentially exposed to chromite ore (NIOSH, 1984). The NOES also estimated that a total of 196,725 workers, including 31,444 women, were potentially exposed to hexavalent chromium(VI) compounds (barium chromate, calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate). Occupational airborne chromium concentrations have declined significantly during the past decades because of improved emission controls. Occupational exposure, which can be two orders of magnitude greater than that to the general populations, occurs mainly from stainless steel production and welding, chromate production, chrome plating, ferrochrome alloys, chrome pigment, and tanning industries. Occupational exposure is due to the soluble and insoluble fractions of chromium(III) and chromium(VI), depending upon the industry. The typical concentration ranges of chromium(VI) in these industries are: stainless steel welding, 50-400 $\mu g/m^3$; chromate production, 100-500 $\mu g/m^3$; chrome plating, 5-25 $\mu g/m^3$; ferrochrome alloys, 10-140 $\mu g/m^3$; and chrome pigment, 60-600 $\mu g/m^3$ (ATSDR, 1993-K014). In a study assessing external and internal chromium exposure among stainless steel welders and mild steel welders, all chromium biological (blood, plasma, and urine) values were found to be higher among the former group, particularly those in the manual metal arc welding process. The higher levels are the result of very significant concentrations of total soluble chromium, mainly hexavalent chromium, in the fumes; the ratio of hexavalent soluble chromium to total water-soluble chromium was about 61% (Edmé et al., 1997). In the tanning industry, exposure is almost exclusively to soluble chromium(III), typically in the range of 10-50 $\mu g/m^3$ (ATSDR, 1993-K014). ACGIH has designated the following threshold limit values (TLVs) as 8-hr time-weighted averages (TWAs) for chromium compounds, as chromium: 0.5 mg/m^3 for chromium(VI) compounds, and 0.05 mg/m^3 for lead chromate, water soluble chromium(VI) compounds, and certain water insoluble chromium(VI) compounds (ACGIH, 1996).

The general population can be exposed to chromium through the air, water, soils and food. The mean daily dietary intake of chromium from air, water, and food is approximately < 02-0.4, 2.0, and 60 µg, respectively (ATSDR, 1993-K014). The Toxic Chemical Release Inventory (EPA) listed 929 industrial facilities that produced, processed, or otherwise used chromium in 1988 (TRI, 1990). In compliance with the Community Right-to-Know Program, the facilities reported releases of chromium to the environment which were estimated to total 9.9 million lb. The atmospheric chromium concentration in the United States is typically < 0.01 $\mu g/m^3$ in rural areas and 0.01-0.03 $\mu g/m^3$ in urban areas. In the United States it was calculated that 64% of the atmospheric chromium emissions, which originate from coal, contain 1.5 to 54 ppm chromium (Merian, 1984). It is been reported that tap water contains 0.4 to 8.0 µg chromium/L with a mean value of 1.8 µg/L (ATSDR, 1993-K014). The chromium concentration in rivers and lakes is usually between 1 and 10 µg/L. The earth's crust and rocks contain about 100 ppm chromium; soils contain, on the average, about 400 ppm (Merian, 1984). Typical chromium levels in most fresh foods are low. Chromium has been detected in vegetables, fruits, grains, cereals, eggs, meat, and fish at concentrations between 20 and 520 µg/kg (ATSDR, 1993-K014).

REGULATIONS

In FY 1982, CPSC investigated the potential hazard to consumers from chromium-containing inks, printed products, and nonprinted consumer products. Although chromium was present in some inks used in printed products, the levels found in the final products did not warrant further investigation.

EPA regulates chromium and its compounds under the Clean Water Act (CWA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), Superfund Amendments and Reauthorization Act (SARA), and Toxic Substances Control Act (TSCA). CERCLA establishes reportable quantities (RQs) for chromium and some chromium compounds. RCRA and SARA subject chromium and its compounds to report/recordkeeping requirements. EPA's Carcinogen Assessment Group includes 10 chromium compounds on its list of potential carcinogens. FDA regulates the use of chromium as indirect food and color additives, in beverages, and in dental devices, and chromic oxide in drugs and cosmetics. NIOSH recommends an exposure limit of 1 $\mu g/m^3$ for chromic acid and chromates and recommends an exposure limit of 500 $\mu g/m^3$ as a 10-hr time-weighted average (TWA) for chromium (II and III) compounds and chromium metal (NIOSHc, 1996). OSHA adopted an 8-hr TWA permissible exposure limit (PEL) of 0.5 mg/m^3 for chromium(II) and chromium(III) compounds and l mg/m^3 for chromium metal; for chromic acid and chromate, the PEL varies with the compound. A ceiling of 0.1 ppm, however, is given. OSHA regulates chromium and certain chromium compounds under the Hazard Communication Standard and hexavalent chromium compounds as chemical hazards in laboratories. Regulations are summarized in Volume II, Table A-16.